Compilation and critical analysis of thermodynamic data for ternary alloy systems

I. Ansara, J.P. Bros, P. Spencer

INSTITUT NATIONAL POLYTECHNIQUE DE GRENOBLE

LABORATOIRE DE THERMODYNAMIQUE ET PHYSICO-CHIMIE METALLURGIQUES

COMPILATION AND CRITICAL ANALYSIS OF THERMODYNAMIC DATA FOR TERNARY ALLOY SYSTEMS

by

I. ANSARA, J.P. BROS and P. SPENCER

(presented at the IVth International CODATA conference TSACHKADZOR, Armenia Republic, U.S.S.R., 24-27 June 1974)

REFERENCE RAPPORT LTPCM-1974-TM-04

ENSEEG-B.P.44-38401 ST.MARTIN D'HERES-FRANCE

COMPILATION AND CRITICAL ANALYSIS OF THERMODYNAMIC DATA FOR TERNARY ALLOY SYSTEMS

by

I. ANSARA, J.P. BROS* and P. SPENCER**

* U.E.R. Chimie - Université de Provence - Place V. Hugo, 13003 Marseille, France.

** National Physical Laboratory, Teddington, Middlesex,U.K.

The thermodynamic approach in resolving industrial problems concerned with high temperature has led, in the two last decades, to a notable development of both theoretical and experimental studies on multicomponent systems. Phase diagram determinations of metallic systems are still carried out very extensively because of their importance in the field of material science, mainly in steelmaking, non-ferrous metallurgy, crystal growth, electroslag-refining, nuclear materials, etc...

These phase diagrams,usually determined by classical methods such as thermal analysis, X-ray cristallography, equilibrium techniques, are established in relatively small composition and temperature ranges. It is obvious that a complete study of such multicomponent systems, useful for the scientist, is tedious and time-consuming. These experimental results have been reviewed in the compilations published by Janecke[1], Rudy[2], Agaev[3], Guertler[4], and it is desirable that such reviews continue.

Phase diagrams calculated from the thermodynamic properties of mixing are less numerous because of the lack of experimental determinations of such properties for ternary systems, although there has been extensive work on the prediction of phase boundaries obtained from the limiting binary systems[5-23].

These two approaches, which can be reconciled through thermodynamic principles, have most of the time been carried out independently neglecting the thermodynamic data relative to the multicomponent solution phase. And yet, from the literature, it can be seen that measurements of the thermodynamic properties of mixing mainly in homogeneous metallic multicomponent phases has been increasing in recent years, the results of which permit a more complete description of a system.

At the second and third CODATA Conferences[24,25] an international cooperative research program dealing with the compilation, critical evaluation and computer storage of the thermodynamic properties of the elements,

inorganic compounds and solution phases was described. In relation to this program, a project for the compilation, evaluation and tabulation of the thermodynamic properties of ternary metallic systems is described in this paper. This project excludes, for the time being non-metallic systems, salt and oxide systems.

The aim of this project is to achieve a uniform presentation of the thermodynamic data for alloys and therefore :

- obtain missing binary data by extrapolation of the ternary values
- compute ternary and multicomponent phase diagrams
- correlate thermodynamic data with experimental phase diagrams
- investigate the influence of a third element on a binary system from the view point of bond mechanism.

At the moment, experimental data for multicomponent systems are presented in variety of ways, for example :

- tables of $\Delta\bar{G}_i = f(T, x_i, x_j/x_k, \ldots)$
- tables of $\Delta\bar{G}_i = f(T, x_i, x_j, x_k \ldots)$
- analytical expressions for $\Delta\bar{G}_i$, ΔH, etc... derived from various physico-chemical models or more simply, from surface fitting
- graphical representation.

Moreover, in integrating the Gibbs-Duhem equation for the partial properties of solution, a number of methods are available[26-30], all of which usually require limiting binary data. Precise details of the binary data and procedures actually used are rarely given in published papers. Similar remarks also apply in respect of the interpolation and differentiation of experimental integral quantities.

A feature which is rarely achieved is the consistency between the thermodynamic properties of solution and ternary phase equilibria. This is

due, not only to the lack of complete information on these two properties but also to the complexity of the problem.

These considerations have led us to discuss the numerical treatment of the experimental data for the multicomponent systems. The main problem is the choice of the interpolation formula used to describe an integral thermodynamic function for such a system. In a general way, an integral excess function Y of solution for a ternary system can be written as follows :

$$Y = \sum_i \sum_j \alpha Y_{ij} + x_i x_j (1 - x_i - x_j) P(x_i, x_j) \qquad (1)$$

where Y_{ij} denotes the excess function of the binary system i-j, in tabular or analytical form, $P(x_i, x_j)$ an equation expressing a ternary interaction contribution, α a weighting factor on the binary quantity which varies according to the model used[31-41]. Partial quantities can be derived from equation (1) and used to fit the experimental data. Normally, the values of Y_{ij} are constrained by the limiting binary data, and it is the coefficients of $P(x_i, x_j)$ which are obtained by the fitting procedure.

From our experience in fitting experimental data for multicomponent solution we recommend that :

- care should be taken to use critically evaluated data for the limiting binary systems ; such data are available in handbooks for example the ones published by Hultgren, and Kubaschewski [42,43]

- different equations, semi-empirical or preferentially derived from statistical thermodynamic be tried in order to reduce the number of parameters in $P(x_i, x_j)$

- if suitable analytical expressions cannot be found, tables of discrete values be used together with spline function interpolation. To illustrate that, minimization of the Gibbs energy in a multicomponent system no longer requires differentiation of that function with respect to its independent variables as simplex methods[44] are now readily available

- whenever possible, phase diagrams are calculated and compared with the experimental ones

- if different sets of experimental data are available, critical evaluation be attempted.

These recommendations and procedures have long been applied for the critical evaluation of binary solution data but not always followed by experimental scientists.

Naturally, for multicomponent systems, the introduction of additional dimensions increases the difficulty and the effort required for critical evaluation, so that it is important to simplify computing procedures.

The application of the above principles is demonstrated for three ternary solutions, Cu-Fe-Ni, Ga-In-Zn, Ga-Sn-Zn in the appendix. In this treatment, the following aspects are covered.

1) Description and analysis of the experimental thermodynamic properties of the ternary system, reference being made to the experimental phase diagram.

2) Fitting of ternary data with different constraints on the binary data. Comparison between experimental and calculated values.

3) Comparison between experimental and calculated phase diagram derived from the thermodynamic data of solution.

4) Tables of the data for partial and integral heats and excess entropies of mixing.

5) Bibliography.

The above presentation is one possible procedure when sufficient information is available. Normally, however, experimental data exist only in a

limited composition range and this procedure will not be possible in its entirety. In such cases, it is envisaged that this limited information be compiled and tabulated to await supplementary data.

The authors are aware that this form of presentation of data can be modified and comments and criticism will be greatly appreciated. Nevertheless, with more and more experimental work being undertaken in multicomponent systems, such a project, in some form, could contribute to the compilation, evaluation, tabulation of thermodynamic properties not only for alloys systems but also for oxides or salts mixtures for which much experimental data are already available.

The project described above is closely related to another international project CALPHAD (calculation of phase diagrams in multicomponent systems), in which American, British, French, German and Swedish scientists participate. One of their main interests is the analysis, critical evaluation and publication of consistent thermodynamic data and phase diagrams for binary systems. Such data will be used for the assessment and prediction of thermodynamic data and phase diagrams for ternary systems. A sample pamphlet for ten binary and three ternary systems is being prepared and will be diffused for criticism.

The assessment and publication of data for multicomponent systems is an ambitious task. However, it is felt that with the increasing use of computer techniques, a relatively modest effort in this field would provide a method of making readily available to the scientific community the fruits of expensive experimental work, which is often at present difficult to exploit satisfactorily.

BIBLIOGRAPHY

(1) E. JÄNECKE, "Handbuch aller Legierungen", Universitätsverlag, Heidelberg, 1949.

(2) E. RUDY, "Ternary Phase Equilibria in Transition Metal-Boron-Carbon-Silicon Systems, Part V Compendium of Phase diagram Data" Tech. Rep. AFML-TR-65-2, 1969, Aerojet General Corp., Sacramento, Calif., U.S.A.

(3) N.V. AGAEV, "Phase Diagrams of Metallic Systems", 1955-1975, Inst. Inf. Sci. Techn., Moscov, URSS.

(4) W. GUERTLER, M. GUERTLER and E. ANASTASIADIAS, "A compendium of Constitutional Ternary Diagrams of Metallic Systems", WADC Tech. Rep. 58-615, 1969, U.S. Dept. Commerce, Springfield Va. 22151, U.S.A.

(5) O. KUBASCHEWSKI, G. WAINWRIGHT, F.J. KIRBY, J. Inst. Met., 1960, 89, 66.

(6) J.L. MEIJERING, Philip Res. Rep. 1951, 6, 183.

(7) L. KAUFMAN and H. BERNSTEIN,"Computer Calculation of Phase Diagrams", Academic Press, N.Y., 1970.

(8) H. GAYE, "Computer Applications of the Thermodynamic of Multicomponent Solutions", Ph. D. Thesis, Carnegie Mellon Univ., Pittsburgh, Pa., U.S.A., 1971.

(9) J.F. COUNSELL, E.B. LEES and P.J. SPENCER, "Metallurgical Chemistry", Proc. Symp. 1971, Ed. O. Kubaschewski, HMSO, U.K., 1971, p. 451.

(10) I. ANSARA, "Metallurgical Chemistry", Proc. Symp. 1971, Ed. O. Kubaschewski, HMSO, U.K., 1971, p. 403.

(11) J.L. MEIJERING, Acta Met., 1957, 5, 257.

(12) M. GAMBINO, J.P. BROS and I. ANSARA, "Thermochimie", Coll. Int. CNRS, N° 201, 1971, Marseille, France, p. 273.

(13) M. GAMBINO, J.P. BROS, and I. ANSARA, Rev. Int. Htes Temp. et Réfract., 1973, 10, 5.

(14) H. GAYE and C.H.P. LUPIS, Scripta Met., 1970, 4, 685.

(15) G. KIRCHNER and B. UHRENIUS, Acta Met., 1971, 22, 523.

(16) L. KAUFMAN and H. NESOR, "Computer Analysis of Alloys Systems", Tech. Rep. AFML-TR-73-56, Manlabs Inc., Cambridge, Mass., USA

(17) I. ANSARA, P. DESRÉ and E. BONNIER, C.R. Acad. Sci., 1970, 270, 1098.

(18) G.B. STRINGFELLOW and P.E. GREENE, J. Phys. Chem. Solids, 1969, 30, 1779.

(19) G.B. STRINGFELLOW and P.E. GREENE, J. Electrochem. Sol. Solid State Sci., 1970, 117, 1075.

(20) A. LAUGIER, Rev. Phys. Appl., 1973, 8, 3, 259.

(21) A.S. JORDAN, Met. Trans., 1971, 2, 1965.

(22) Y.A. CHANG and D. NAUJOCK, Met. Trans., 1972, 3, 1693.

(23) J.F. COUNSELL, E.B. LEES and P.J. SPENCER, DCS Rep. 9, NPL, 1970, Teddington U.K.

(24) Second Int. CODATA Conference, held in St Andrews Scotland (U.K.), Sept. 1971 (no proceedings have been published).

(25) E. BONNIER, Third Int. Codata Conf., Le Creusot France, Pub. CODATA, Frankfurt/Main, BRD.

(26) L.S. DARKEN, J. Amer. Chem. Soc., 1950, 72, 2909.

(27) C. WAGNER, "Thermodynamic of Alloys", Addison Wesley Pub. Co. Inc., Mass., 1952.

(28) R. SCHUMANN, Acta Met., 1955, 3, 219.

(29) N.A. GOKCEN, J. Phys. Chem., 1960, 64, 401.

(30) N.A. GOKCEN, Aerospace Corp., Rept. N° TR-0059 (6210-10), 2, 1971, L.A., U.S.A.

(31) F. KOHLER, Monat. Für Chemie, 1960, 91, 738.

(32) G.W. TOOP, Trans. Met. Soc. AIME, 1965, 233, 850.

(33) E. BONNIER and R. CABOZ, C.R. Acad. Sci., 1960, 250, 527.

(34) B. BRION, J.C. MATHIEU, P. HICTER and P. DESRÉ, J. Chim. Phys., 1969, 66, 238.

(35) B. BRION, J.C. MATHIEU, and P. DESRÉ, J. Chim. Phys., 1970, 67, 1745.

(36) I. ANSARA, E. BONNIER and J.C. MATHIEU, Z.für Metallkde, 1973, 64, 4, 258.

(37) C.H.P. LUPIS, Ph. D. Thesis, MIT, Boston 1965.

(38) C.H.P. LUPIS and J.F. ELLIOTT, Acta Met., 1967, 15, 265.

(39) K. WOHL, Trans. Amer. Inst. Chem. Eng., 1946, 42, 215.

(40) H. KEHIAIAN, Bull. Acad. Pol. Sci., 1966, 14, 153.

(41) C. COLINET, DES, Fac. Sci., Univ. Grenoble, France, 1967.

(42) R. HULTGREN, P.D. DESAI, D.T. HAWKINS, M. GLEISER and K.K. KELLEY, "Selected Values of the Thermodynamic Properties of Binary Alloys", 1973, Amer. Soc. for Metals, Metals Park, Ohio, U.S.A.

(43) O. KUBASCHEWSKI, E.LL. EVANS and C.B.J. ALCOCK, "Metallurgical Thermochemistry", Pergamon Press, 1967, U.K.

(44) J.A. NELDER and R. MEAD, Comp. J., 1965, 308.

A P P E N D I X

The thermodynamic functions refer to a mole of $A_{(x)}\ B_{(1-x)}$

x molar fraction

ΔH, $\Delta \bar{H}_i$, $\Delta \bar{G}_i$ are expressed in $cal.mol^{-1}$

ΔS^{xs}, ΔS_i^{xs} are expressed in $cal.mol^{-1}K^{-1}$

Temperature in K

1 cal = 4,184 J.

Ga-In-Zn

I - EXPERIMENTAL RESULTS.-

The heats of mixing of the liquid solutions have been measured by microcalorimetry[1] at 723 K for :

$$0 < x_{In} < 0.8 \quad ; \quad x_{Ga}/x_{Zn} = 1/3 \; ; \; 1/1 \; ; \; 3/1$$

and $$0 < x_{Zn} < 0.8 \quad ; \quad x_{Ga}/x_{In} = 1/3 \; ; \; 1/1 \; ; \; 3/1$$

The partial free energies have been determined[2] by an e.m.f. method in the temperature range $693 < T < 793$ K for :

$$0.1 < x_{In} < 0.9 \quad ; \quad x_{Ga}/x_{In} = 3/17 \; ; \; 1/3 \; ; \; 3/1 \; ; \; 1/1 .$$

II - COMPARISON BETWEEN EXPERIMENTAL AND CALCULATED THERMODYNAMIC DATA.-

a) Binary solutions :

Ga-In[3]

$$\begin{cases} \Delta H_M = x_{In}(1 - x_{In})(1060) \\ \Delta S_M^{xs} = x_{In}(1-x_{In})(-0.43397\, x_{In}^2 - 0.00676\, x_{In} - 0.30651) \end{cases}$$

Ga-Zn[1]

$$\begin{cases} \Delta H_M = x_{Zn}(1-x_{Zn})(420\, x_{Zn}^2 + 478.0\, x_{Zn} + 1413.0) \\ \Delta S_M^{xs} = x_{Zn}(1-x_{Zn})(-9.18456\, x_{Zn}^3 + 13.08382\, x_{Zn}^2 \\ \qquad - 5.35968\, x_{Zn} + 2.49791) \end{cases}$$

In-Zn[4]

$$\begin{cases} \Delta H_M = x_{Zn}(1-x_{Zn})(2473.5605\, x_{Zn}^3 - 2324.8502\, x_{Zn}^2 \\ \qquad + 1469.9522\, x_{Zn} + 2588.1589) \\ \Delta S_M^{xs} = x_{Zn}(1-x_{Zn})(0.20367\, x_{Zn} + 1.06355) \end{cases}$$

b) Ternary solutions :

The following equation :

$$\Delta H_M = (x_{In} + x_{Zn})^2 (\Delta H_{In-Zn}) x_{In}/x_{Zn} + (x_{Ga} + x_{Zn})^2 (\Delta H_{Ga-Zn}) x_{Ga}/x_{Zn}$$

$$+ (x_{Ga} + x_{In})^2 (\Delta H_{Ga-In}) x_{Ga}/x_{In}$$

fits within 25 cal the experimental data as shown in table I.

The partial free energies at 743 K derived from the combination of the heats and excess entropies using a similar equation are in very good agreement with the experimental values as shown in table II.

Table I

Calculated and experimental ΔH_M at 723 K (cal/mol)

x_{Ga}/x_{Zn} / x_{In}	1/3		1/1		3/1	
	exp	exp-calc	exp	exp-calc	exp	exp-calc
0.1	570	-11	580	-15	380	- 3
0.2	680	-15	640	-13	430	- 6
0.3	740	- 3	675	-24	455	- 9
0.4	750	- 4	670	-26	460	- 8
0.5	725	- 5	635	-29	450	3
0.6	655	7	565	-26	410	7
0.7	545	8	450	- 6	340	4
0.8	400	10	320	0	259	13
0.9	220	11	175	3	130	- 4

x_{Ga}/x_{In} / x_{Zn}	1/3		1/1		3/1	
	exp	exp-calc	exp	exp-calc	exp	exp-calc
0.1	390	8	410	- 2	335	- 9
0.2	540	1	540	- 8	445	- 9
0.3	665	- 7	635	- 8	535	-10
0.4	740	- 5	700	-10	600	-14
0.5	770	- 4	720	- 5	620	- 7
0.6	750	- 2	695	0	605	- 6
0.7	675	0	620	2	550	-13
0.8	540	- 4	480	8	415	6
0.9	310	7	270	13	240	3

Table II

Calculated and experimental $\Delta\bar{G}_{Zn}$ at 743 K (cal/mol)

x_{Ga}/x_{In} / x_{Zn}	3/17		1/3		1/1		3/1	
	exp	exp-calc	exp	exp-calc	exp	exp-calc	exp	exp-calc
0.1	-1995	125	-2202	99	-2495	-175	-2696	280
0.2	-1240	32	-1187	262	-1625	-123	-1890	34
0.3	- 873	- 20	- 939	49	-1161	- 96	-1320	87
0.4	- 608	- 6	- 694	- 10	- 869	- 22	- 983	70
0.5	- 461	- 29	- 509	- 34	- 645	34	- 737	25
0.6	- 345	- 33	- 382	- 47	- 482	70	- 559	- 38
0.7	- 272	- 42	- 296	- 52	- 345	- 62	- 419	- 82
0.8	- 188	- 18	- 205	- 26	- 233	- 37	- 275	- 66
0.9	- 115	- 8	- 112	- 1	- 126	- 10	- 137	- 23

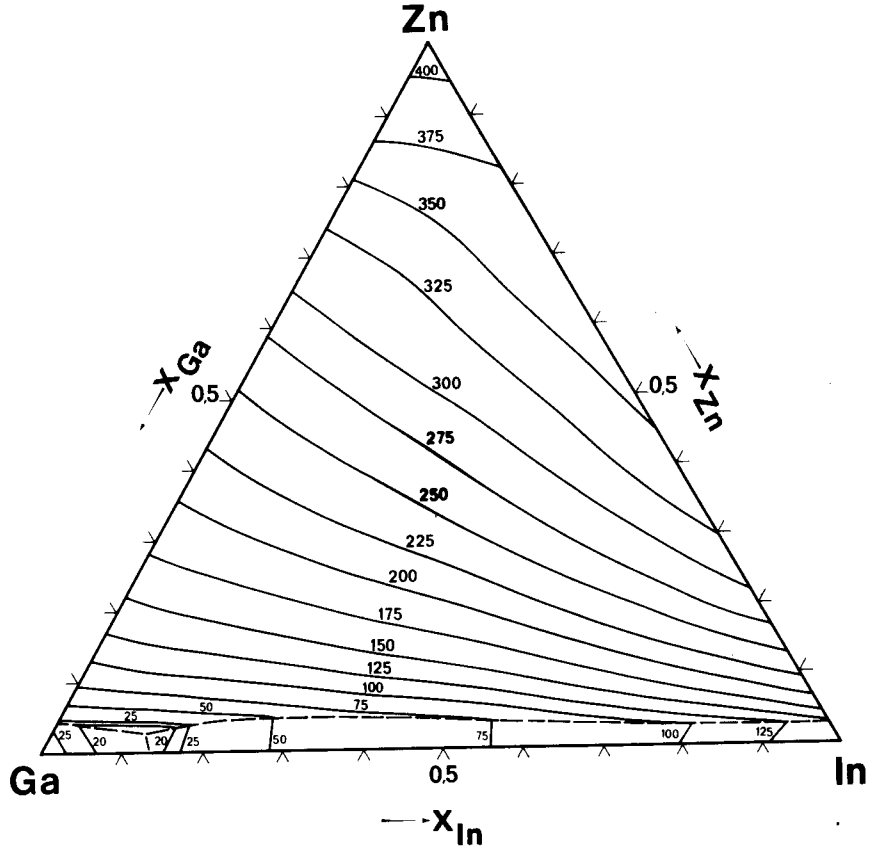
III - PHASE DIAGRAM.-

The phase diagram of the three limiting binary systems are of a eutectic type with no significant solid solubility. The properties defined above enables the liquidus on the Zn rich side to be calculated. These temperatures (K) are compared in table III to those which are derived from the e.m.f. measurements[2].

Table III

x_{Ga}/x_{In} / x_{Zn}	3/17		1/3		1/1		3/1	
	ref(2)	exp-calc.	ref(2)	exp-calc.	ref(2)	exp-calc.	ref(2)	exp-calc.
0.1	471	- 5	443	- 2	405	2	380	6
0.2	530	- 1	508	- 1	462	- 6	437	- 1
0.3	560	- 9	544	- 8	506	- 4	476	- 4
0.4	588	- 5	570	- 7	536	- 6	511	- 4
0.5	603	- 7	590	- 7	560	-12	539	- 4
0.6	615	- 8	604	-10	581	-11	563	-12
0.7	625	- 7	616	- 9	603	- 8	585	-14
0.8	638	- 3	632	- 7	623	-12	614	-13
0.9	654	- 7	655	- 4	650	- 7	647	-10

Since the differences are smaller than 15 K, the phase diagram which is shown in the following figure has been computed (the temperatures are in °C).


Zn
400
375
350
325
300
275
250
225
200
175
150
125
100
75
50
25
20
20
25
50
75
100
125
x_{Ga}
0,5
x_{Zn}
0,5
Ga
0,5
In
x_{In}

PARTIAL AND INTEGRAL HEATS OF MIXING FOR LIQUID GA-IN-ZN SOLUTIONS AT 723K (CAL/MOL)

X ZN	XGA/XIN	DH ZN	DH GA	DH IN	DH
0.0	9.000	1435	11	859	95
0.1	9.000	1314	13	915	224
0.2	9.000	1151	34	1019	336
0.3	9.000	969	82	1194	426
0.4	9.000	779	169	1439	490
0.5	9.000	591	308	1747	521
0.6	9.000	411	511	2115	515
0.7	9.000	251	796	2542	467
0.8	9.000	121	1179	3030	369
0.9	9.000	33	1677	3583	216
1.0	9.000	0	2311	4206	0
0.0	4.000	1478	42	678	170
0.1	4.000	1371	36	742	296
0.2	4.000	1209	49	836	407
0.3	4.000	1030	90	972	495
0.4	4.000	834	172	1177	557
0.5	4.000	632	308	1463	586
0.6	4.000	438	513	1834	574
0.7	4.000	265	803	2293	515
0.8	4.000	126	1189	2841	404
0.9	4.000	33	1688	3478	235
1.0	4.000	0	2311	4206	0
0.0	2.333	1543	95	519	223
0.1	2.333	1443	77	588	351
0.2	2.333	1266	78	689	462
0.3	2.333	1080	112	819	551
0.4	2.333	879	189	1003	612
0.5	2.333	670	323	1265	638
0.6	2.333	465	529	1624	622
0.7	2.333	281	819	2091	557
0.8	2.333	133	1206	2675	436
0.9	2.333	35	1700	3379	252
1.0	2.333	0	2311	4206	0
0.0	1.500	1629	170	382	254
0.1	1.500	1530	135	452	389
0.2	1.500	1334	123	558	504
0.3	1.500	1130	147	692	595
0.4	1.500	919	220	870	655
0.5	1.500	703	352	1117	680
0.6	1.500	491	557	1461	662
0.7	1.500	298	846	1926	592
0.8	1.500	142	1229	2530	463
0.9	1.500	38	1715	3287	268
1.0	1.500	0	2311	4206	0

0.0	1.000	1736	265	265	265
0.1	1.000	1630	211	335	408
0.2	1.000	1414	182	441	532
0.3	1.000	1185	196	581	627
0.4	1.000	957	264	759	690
0.5	1.000	732	394	999	714
0.6	1.000	515	598	1331	694
0.7	1.000	316	882	1788	622
0.8	1.000	152	1257	2401	488
0.9	1.000	41	1731	3200	283
1.0	1.000	0	2311	4206	0
0.0	0.667	1864	382	170	254
0.1	0.667	1745	304	235	411
0.2	0.667	1504	257	339	546
0.3	0.667	1245	260	481	649
0.4	0.667	997	323	663	715
0.5	0.667	760	452	901	741
0.6	0.667	538	651	1224	721
0.7	0.667	334	929	1672	646
0.8	0.667	164	1292	2288	509
0.9	0.667	45	1749	3118	298
1.0	0.667	0	2311	4206	0
0.0	4.286	1473	38	697	163
0.1	4.286	1364	33	760	290
0.2	4.286	1203	46	853	400
0.3	4.286	1024	88	992	489
0.4	4.286	829	170	1200	551
0.5	4.286	628	307	1488	579
0.6	4.286	435	513	1861	568
0.7	4.286	263	801	2318	511
0.8	4.286	125	1188	2860	401
0.9	4.286	33	1687	3489	233
1.0	4.286	0	2311	4206	0
0.0	2.500	1532	87	541	216
0.1	2.500	1432	70	609	345
0.2	2.500	1258	73	709	455
0.3	2.500	1073	108	839	544
0.4	2.500	873	186	1025	605
0.5	2.500	665	320	1290	631
0.6	2.500	461	526	1651	616
0.7	2.500	278	816	2118	551
0.8	2.500	132	1203	2698	431
0.9	2.500	35	1698	3393	250
1.0	2.500	0	2311	4206	0
0.0	0.111	2375	859	11	95
0.1	0.111	2157	700	44	314
0.2	0.111	1808	614	123	499
0.3	0.111	1450	598	257	639
0.4	0.111	1128	646	445	730
0.5	0.111	850	752	686	771
0.6	0.111	608	915	998	761
0.7	0.111	393	1139	1419	692
0.8	0.111	206	1433	2018	556
0.9	0.111	61	1815	2900	334
1.0	0.111	0	2311	4206	0

PARTIAL AND INTEGRAL EXCESS ENTROPIES OF MIXING FOR LIQUID GA-IN-ZN SOLUTIONS AT 723K (CAL/MOL)/K

X ZN	XGA/XIN	SXS ZN	SXS GA	SXS IN	SXS
0.0	9.000	2.3825	-0.0023	-0.2599	-0.0280
0.1	9.000	1.3968	0.0515	-0.3014	0.1543
0.2	9.000	1.0489	0.1114	-0.2656	0.2688
0.3	9.000	0.9092	0.1549	-0.1988	0.3565
0.4	9.000	0.7686	0.2309	-0.1112	0.4255
0.5	9.000	0.5681	0.4030	0.0062	0.4657
0.6	9.000	0.3350	0.7040	0.1691	0.4612
0.7	9.000	0.1307	1.1010	0.3888	0.4004
0.8	9.000	0.0090	1.4684	0.6635	0.2848
0.9	9.000	-0.0169	1.5685	0.9720	0.1357
1.0	9.000	-0.0000	1.0375	1.2672	0.0000
0.0	4.000	2.2631	-0.0072	-0.2312	-0.0520
0.1	4.000	1.3463	0.0526	-0.2699	0.1239
0.2	4.000	1.0536	0.1058	-0.2411	0.2398
0.3	4.000	0.9200	0.1468	-0.1833	0.3325
0.4	4.000	0.7590	0.2368	-0.1014	0.4051
0.5	4.000	0.5408	0.4336	0.0155	0.4454
0.6	4.000	0.3074	0.7508	0.1808	0.4391
0.7	4.000	0.1173	1.1355	0.4017	0.3787
0.8	4.000	0.0105	1.4598	0.6731	0.2689
0.9	4.000	-0.0123	1.5193	0.9743	0.1300
1.0	4.000	-0.0000	1.0375	1.2672	0.0000
0.0	2.333	2.1406	-0.0145	-0.2096	-0.0730
0.1	2.333	1.2969	0.0508	-0.2427	0.0962
0.2	2.333	1.0575	0.0968	-0.2183	0.2133
0.3	2.333	0.9231	0.1398	-0.1678	0.3102
0.4	2.333	0.7397	0.2502	-0.0901	0.3848
0.5	2.333	0.5080	0.4736	0.0269	0.4238
0.6	2.333	0.2801	0.8009	0.1944	0.4156
0.7	2.333	0.1068	1.1635	0.4152	0.3565
0.8	2.333	0.0137	1.4393	0.6819	0.2534
0.9	2.333	-0.0076	1.4629	0.9758	0.1248
1.0	2.333	-0.0000	1.0375	1.2672	0.0000
0.0	1.500	2.0150	-0.0266	-0.1873	-0.0909
0.1	1.500	1.2518	0.0431	-0.2143	0.0713
0.2	1.500	1.0600	0.0823	-0.1934	0.1896
0.3	1.500	0.9158	0.1344	-0.1488	0.2895
0.4	1.500	0.7095	0.2725	-0.0738	0.3642
0.5	1.500	0.4707	0.5217	0.0440	0.4007
0.6	1.500	0.2545	0.8500	0.2123	0.3907
0.7	1.500	0.0999	1.1795	0.4310	0.3340
0.8	1.500	0.0187	1.4032	0.6912	0.2387
0.9	1.500	-0.0030	1.3984	0.9772	0.1203
1.0	1.500	-0.0000	1.0375	1.2672	0.0000

0.0	1.000	1.8853	-0.0495	-0.1597	-0.1046
0.1	1.000	1.2126	0.0236	-0.1812	0.0503
0.2	1.000	1.0579	0.0587	-0.1638	0.1696
0.3	1.000	0.8939	0.1307	-0.1236	0.2707
0.4	1.000	0.6677	0.3035	-0.0497	0.3432
0.5	1.000	0.4308	0.5740	0.0688	0.3761
0.6	1.000	0.2325	0.8901	0.2364	0.3648
0.7	1.000	0.0971	1.1754	0.4501	0.3118
0.8	1.000	0.0253	1.3467	0.7017	0.2251
0.9	1.000	0.0014	1.3244	0.9789	0.1164
1.0	1.000	-0.0000	1.0375	1.2672	0.0000
0.0	0.667	1.7493	-0.0921	-0.1253	-0.1120
0.1	0.667	1.1796	-0.0167	-0.1420	0.0352
0.2	0.667	1.0445	0.0223	-0.1282	0.1545
0.3	0.667	0.8527	0.1294	-0.0905	0.2540
0.4	0.667	0.6149	0.3406	-0.0163	0.3218
0.5	0.667	0.3911	0.6206	0.1025	0.3504
0.6	0.667	0.2158	0.9077	0.2668	0.3388
0.7	0.667	0.0985	1.1396	0.4727	0.2908
0.8	0.667	0.0329	1.2636	0.7135	0.2131
0.9	0.667	0.0055	1.2393	0.9812	0.1134
1.0	0.667	0.0000	1.0375	1.2672	0.0000
0.0	4.286	2.2761	-0.0066	-0.2338	-0.0496
0.1	4.286	1.3517	0.0526	-0.2730	0.1271
0.2	4.286	1.0531	0.1065	-0.2437	0.2428
0.3	4.286	0.9191	0.1476	-0.1850	0.3350
0.4	4.286	0.7605	0.2358	-0.1025	0.4073
0.5	4.286	0.5440	0.4299	0.0144	0.4476
0.6	4.286	0.3104	0.7455	0.1795	0.4416
0.7	4.286	0.1186	1.1320	0.4003	0.3811
0.8	4.286	0.0102	1.4613	0.6721	0.2706
0.9	4.286	-0.0128	1.5249	0.9741	0.1306
1.0	4.286	-0.0000	1.0375	1.2672	0.0000
0.0	2.500	2.1583	-0.0132	-0.2126	-0.0702
0.1	2.500	1.3038	0.0513	-0.2465	0.1000
0.2	2.500	1.0570	0.0983	-0.2216	0.2169
0.3	2.500	0.9232	0.1407	-0.1702	0.3133
0.4	2.500	0.7431	0.2478	-0.0920	0.3877
0.5	2.500	0.5130	0.4673	0.0250	0.4270
0.6	2.500	0.2839	0.7936	0.1922	0.4191
0.7	2.500	0.1081	1.1601	0.4131	0.3597
0.8	2.500	0.0131	1.4431	0.6807	0.2556
0.9	2.500	-0.0083	1.4714	0.9756	0.1255
1.0	2.500	-0.0000	1.0375	1.2672	0.0000
0.0	0.111	1.2667	-0.4741	-0.0137	-0.0598
0.1	0.111	1.0326	-0.3609	-0.0168	0.0572
0.2	0.111	0.8173	-0.1511	0.0026	0.1532
0.3	0.111	0.6221	0.0644	0.0508	0.2232
0.4	0.111	0.4586	0.2448	0.1285	0.2675
0.5	0.111	0.3217	0.3946	0.2363	0.2869
0.6	0.111	0.2089	0.5253	0.3751	0.2814
0.7	0.111	0.1195	0.6475	0.5462	0.2505
0.8	0.111	0.0541	0.7695	0.7509	0.1938
0.9	0.111	0.0138	0.8979	0.9908	0.1105
1.0	0.111	0.0000	1.0375	1.2672	0.0000

BIBLIOGRAPHY

(1) M. GAMBINO, J.P. BROS and I. ANSARA, "Thermochimie", Coll. Int. CNRS N° 201, 1971, Marseille, p. 273.

(2) W.J. SVIRBELY and S.M. READ, J. Phys. Chem., 1962, 66, 4, 658.

(3) F.H. HAYES and O. KUBASCHEWSKI, J. Inst. Metal., 1969, 97, 381.

(4) R. HULTGREN, P.D. DESAI, D.T. HAWKINS, M. GLEISER, K.K. KELLEY, "Selected Values of the Thermodynamic Properties of Binary Alloys", 1973, American Soc. for Metals, Metals Park, Ohio, USA

Cu-Fe-Ni

I - EXPERIMENTAL RESULTS.-

The heats of mixing of Cu-Fe-Ni solid solutions have been determined with an adiabatic calorimeter at 1323 K for nine different alloy compositions given in table I.

This ternary system exhibits a miscibility gap in the solid state which has been determined by BRADLEY[2] at 1123 and 1323 K.

II - COMPARISON BETWEEN EXPERIMENTAL AND CALCULATED THERMODYNAMIC DATA.-

a) Binary solutions :

Cu-Ni[3]

$$\Delta H_M = x_{Cu} x_{Ni} [857\, x_{Cu} + 3092\, x_{Ni}]$$

$$\Delta S^{xs} = x_{Cu} x_{Ni} [-1.1642\, x_{Cu} - 0.4970\, x_{Ni}]$$

Fe-Ni[4]

$$\Delta H_M = x_{Fe} x_{Ni} [-6642\, x_{Ni} - 483\, x_{Fe}]$$

$$\Delta S^{xs} = x_{Fe} x_{Ni} [-3.1295\, x_{Ni} + 0.4612\, x_{Fe}]$$

Cu-Fe[1]

$$\Delta H_M = x_{Cu} x_{Fe} [12936\, x_{Fe} + 10107\, x_{Cu}]$$

(derived from the heats of mixing of the ternary solid solutions)

$$\Delta S^{xs} = x_{Cu} x_{Fe} [2.9805\, x_{Cu} + 2.9805\, x_{Fe}]$$

(derived from the binary phase diagram using the extrapolated values of ΔH_M)

b) Ternary solutions :

1) Heats of mixing :

The experimental values of the heats of mixing were fitted by the following equation :

$$\Delta H_M = x_{Cu} x_{Ni} [857\, x_{Cu} + 3092\, x_{Ni}] + x_{Fe} x_{Ni} [-6642\, x_{Ni} - 483\, x_{Fe}]$$

$$+ x_{Cu} x_{Fe} [A\, x_{Fe} + B\, x_{Cu}] + C\, x_{Cu} x_{Fe} x_{Ni}$$

which yields : A = 12936 ; B = 10107 ; C = - 2066

Table I shows that the calculated values are within the experimental error (± 150 cal.mol^{-1}) except for one point.

Table I

x_{Cu}	x_{Ni}	x_{Fe}	exp	exp - calc.
0.050	0.900	0.050	- 283	- 139
0.100	0.800	0.100	- 250	- 33
0.050	0.760	0.190	- 710	- 73
0.190	0.760	0.050	492	313
0.167	0.667	0.167	- 330	- 143
0.200	0.600	0.200	- 51	60
0.110	0.445	0.445	- 245	19
0.445	0.445	0.110	434	- 11
0.333	0.333	0.333	653	- 4

2) Excess entropy of mixing :

The excess entropy of mixing is calculated from the binary data by the following equation :

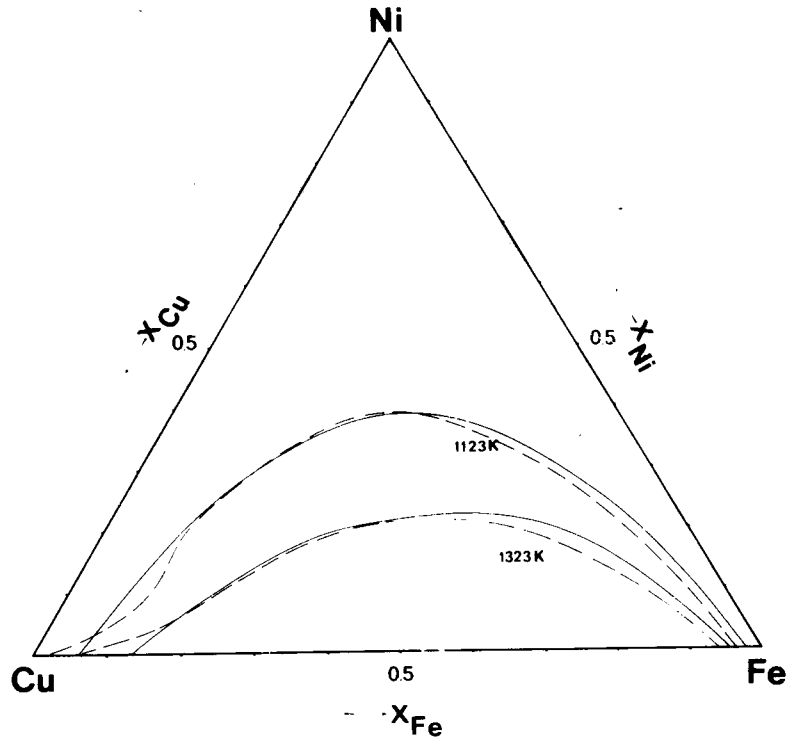
$$\Delta S_M^{xs} = x_{Cu}x_{Ni}\left[-1.1642\,x_{Cu} - 0.4970\,x_{Ni}\right] + x_{Fe}x_{Ni}\left[-3.1295\,x_{Ni} + 0.4612\,x_{Fe}\right]$$

$$+ x_{Cu}x_{Fe}\left[A'\,x_{Cu} + A'\,x_{Fe}\right]$$

A' = 2.9805 (derived from the binary phase diagram using the extrapolated values of ΔH_M).

III - COMPARISON WITH THE EXPERIMENTAL PHASE DIAGRAM.-

The isothermal sections at 1123 and 1323 K are calculated[1] using the above data for the ternary solution and compared to the experimental results in figure 1. A satisfactory agreement is observed .


Ni
x_{Cu}
0.5
0.5
x_{Ni}
1123K
1323K
Cu
0.5
Fe
x_{Fe}

IV -

PARTIAL AND INTEGRAL HEATS OF MIXING FOR SOLID HOMOGENEOUS CU-FE-NI SOLUTIONS AT 1323K (CAL/MOL)

X NI	XCU/XFE	DH NI	DH CU	DH FE	DH
0.0	9.000	-1367	78	8645	935
0.1	9.000	-694	235	6790	742
0.2	9.000	-221	349	4916	611
0.3	9.000	82	448	3057	528
0.4	9.000	246	560	1248	478
0.5	9.000	299	714	-478	445
0.6	9.000	274	936	-2086	413
0.7	9.000	201	1257	-3541	368
0.8	9.000	110	1704	-4809	295
0.9	9.000	33	2306	-5854	177
1.0	9.000	0	3092	-6642	0
0.0	4.000	-3217	336	7193	1708
0.1	4.000	-2175	598	5813	1271
0.2	4.000	-1374	791	4331	936
0.3	4.000	-787	943	2781	687
0.4	4.000	-381	1077	1204	507
0.5	4.000	-126	1223	-363	381
0.6	4.000	9	1406	-1880	293
0.7	4.000	56	1656	-3307	227
0.8	4.000	47	2000	-4604	167
0.9	4.000	18	2469	-5730	96
1.0	4.000	0	3092	-6642	0
0.0	2.333	-4659	808	5784	2301
0.1	2.333	-3362	1104	4835	1674
0.2	2.333	-2323	1325	3716	1176
0.3	2.333	-1518	1491	2463	792
0.4	2.333	-919	1624	1116	505
0.5	2.333	-499	1746	-287	302
0.6	2.333	-229	1881	-1705	166
0.7	2.333	-77	2056	-3093	84
0.8	2.333	-10	2296	-4410	39
0.9	2.333	3	2632	-5608	16
1.0	2.333	0	3092	-6642	0
0.0	1.500	-5659	1527	4453	2697
0.1	1.500	-4229	1779	3880	1938
0.2	1.500	-3048	1968	3090	1321
0.3	1.500	-2099	2107	2115	836
0.4	1.500	-1362	2208	990	468
0.5	1.500	-816	2287	-248	204
0.6	1.500	-436	2364	-1558	32
0.7	1.500	-195	2457	-2899	-62
0.8	1.500	-63	2592	-4225	-89
0.9	1.500	-10	2795	-5489	-65
1.0	1.500	-0	3092	-6642	-0

0.0	1.000	-6184	2527	3234	2880
0.1	1.000	-4753	2646	2974	2050
0.2	1.000	-3533	2738	2471	1364
0.3	1.000	-2519	2801	1749	814
0.4	1.000	-1703	2837	835	391
0.5	1.000	-1071	2852	-239	85
0.6	1.000	-610	2856	-1438	-112
0.7	1.000	-297	2862	-2722	-210
0.8	1.000	-111	2889	-4050	-218
0.9	1.000	-22	2957	-5373	-145
1.0	1.000	-0	3092	-6642	-0
0.0	0.667	-6199	3843	2160	2833
0.1	0.667	-4908	3732	2140	1997
0.2	0.667	-3760	3653	1876	1294
0.3	0.667	-2765	3586	1376	720
0.4	0.667	-1932	3519	658	271
0.5	0.667	-1261	3444	-257	-56
0.6	0.667	-748	3360	-1341	-266
0.7	0.667	-384	3271	-2563	-361
0.8	0.667	-152	3186	-3883	-346
0.9	0.667	-33	3119	-5259	-225
1.0	0.667	-0	3092	-6642	-0
0.0	0.429	-5670	5507	1266	2538
0.1	0.429	-4669	5061	1405	1769
0.2	0.429	-3710	4729	1322	1105
0.3	0.429	-2826	4473	1009	549
0.4	0.429	-2043	4260	467	106
0.5	0.429	-1381	4067	-297	-222
0.6	0.429	-849	3879	-1266	-430
0.7	0.429	-453	3685	-2420	-516
0.8	0.429	-188	3484	-3726	-475
0.9	0.429	-43	3282	-5149	-304
1.0	0.429	-0	3092	-6642	-0
0.0	0.250	-4564	7555	585	1979
0.1	0.250	-4011	6658	794	1352
0.2	0.250	-3367	5986	828	786
0.3	0.250	-2689	5474	660	294
0.4	0.250	-2029	5069	269	-110
0.5	0.250	-1426	4727	-354	-415
0.6	0.250	-911	4414	-1211	-608
0.7	0.250	-504	4104	-2292	-675
0.8	0.250	-217	3783	-3578	-605
0.9	0.250	-52	3444	-5040	-384
1.0	0.250	-0	3092	-6642	-0
0.0	0.111	-2846	10020	152	1139
0.1	0.111	-2909	8549	330	733
0.2	0.111	-2712	7440	411	329
0.3	0.111	-2343	6602	340	-50
0.4	0.111	-1881	5954	72	-380
0.5	0.111	-1392	5428	-426	-637
0.6	0.111	-930	4968	-1173	-798
0.7	0.111	-536	4530	-2178	-838
0.8	0.111	-240	4083	-3437	-735
0.9	0.111	-59	3606	-4935	-463
1.0	0.111	-0	3092	-6642	-0

PARTIAL AND INTEGRAL EXCESS ENTROPIES OF MIXING FOR HOMOGENEOUS SOLID CU-FE-NI SOLUTIONS AT 1323K (CAL/MOL)/K

X NI	XCU/XFE	SXS NI	SXS CU	SXS FE	SXS
0.0	9.000	-1.4749	0.0298	2.4142	0.2682
0.1	9.000	-1.1217	0.0403	2.1357	0.1127
0.2	9.000	-0.8283	0.0228	1.7768	-0.0071
0.3	9.000	-0.5894	-0.0176	1.3445	-0.0938
0.4	9.000	-0.4000	-0.0758	0.8460	-0.1502
0.5	9.000	-0.2546	-0.1465	0.2884	-0.1788
0.6	9.000	-0.1480	-0.2242	-0.3210	-0.1824
0.7	9.000	-0.0748	-0.3037	-0.9750	-0.1636
0.8	9.000	-0.0295	-0.3794	-1.6660	-0.1252
0.9	9.000	-0.0064	-0.4457	-2.3867	-0.0698
1.0	9.000	-0.0000	-0.4970	-3.1295	-0.0000
0.0	4.000	-1.6804	0.1192	1.9075	0.4769
0.1	4.000	-1.3297	0.1396	1.7336	0.2796
0.2	4.000	-1.0242	0.1372	1.4715	0.1184
0.3	4.000	-0.7626	0.1132	1.1263	-0.0077
0.4	4.000	-0.5436	0.0690	0.7034	-0.0999
0.5	4.000	-0.3652	0.0065	0.2083	-0.1592
0.6	4.000	-0.2255	-0.0722	-0.3530	-0.1866
0.7	4.000	-0.1219	-0.1648	-0.9741	-0.1834
0.8	4.000	-0.0519	-0.2685	-1.6485	-0.1504
0.9	4.000	-0.0124	-0.3804	-2.3694	-0.0890
1.0	4.000	-0.0000	-0.4970	-3.1295	-0.0000
0.0	2.333	-1.7808	0.2682	1.4604	0.6259
0.1	2.333	-1.4590	0.2806	1.3740	0.4019
0.2	2.333	-1.1622	0.2803	1.1962	0.2116
0.3	2.333	-0.8941	0.2633	0.9289	0.0559
0.4	2.333	-0.6579	0.2267	0.5749	-0.0645
0.5	2.333	-0.4562	0.1678	0.1376	-0.1487
0.6	2.333	-0.2905	0.0849	-0.3789	-0.1960
0.7	2.333	-0.1621	-0.0230	-0.9697	-0.2056
0.8	2.333	-0.0712	-0.1564	-1.6294	-0.1766
0.9	2.333	-0.0175	-0.3147	-2.3516	-0.1084
1.0	2.333	-0.0000	-0.4970	-3.1295	-0.0000
0.0	1.500	-1.7760	0.4769	1.0730	0.7153
0.1	1.500	-1.5099	0.4632	1.0567	0.4795
0.2	1.500	-1.2426	0.4518	0.9504	0.2724
0.3	1.500	-0.9842	0.4326	0.7519	0.0969
0.4	1.500	-0.7434	0.3968	0.4603	-0.0440
0.5	1.500	-0.5277	0.3370	0.0761	-0.1475
0.6	1.500	-0.3433	0.2469	-0.3990	-0.2106
0.7	1.500	-0.1953	0.1215	-0.9620	-0.2303
0.8	1.500	-0.0874	-0.0429	-1.6086	-0.2037
0.9	1.500	-0.0219	-0.2486	-2.3334	-0.1279
1.0	1.500	-0.0000	-0.4970	-3.1295	-0.0000

0.0	1.000	-1.6660	0.7451	0.7451	0.7451
0.1	1.000	-1.4826	0.6871	0.7816	0.5126
0.2	1.000	-1.2658	0.6514	0.7340	0.3010
0.3	1.000	-1.0332	0.6206	0.5950	0.1155
0.4	1.000	-0.8001	0.5794	0.3593	-0.0384
0.5	1.000	-0.5799	0.5142	0.0236	-0.1555
0.6	1.000	-0.3840	0.4138	-0.4134	-0.2303
0.7	1.000	-0.2217	0.2689	-0.9509	-0.2575
0.8	1.000	-0.1004	0.0719	-1.5863	-0.2318
0.9	1.000	-0.0254	-0.1823	-2.3148	-0.1477
1.0	1.000	-0.0000	-0.4970	-3.1295	-0.0000
0.0	0.667	-1.4508	1.0731	0.4768	0.7153
0.1	0.667	-1.3771	0.9522	0.5482	0.5011
0.2	0.667	-1.2319	0.8790	0.5465	0.2972
0.3	0.667	-1.0413	0.8272	0.4579	0.1116
0.4	0.667	-0.8283	0.7740	0.2717	-0.0478
0.5	0.667	-0.6130	0.6992	-0.0200	-0.1727
0.6	0.667	-0.4126	0.5855	-0.4221	-0.2552
0.7	0.667	-0.2413	0.4189	-0.9365	-0.2872
0.8	0.667	-0.1103	0.1880	-1.5624	-0.2607
0.9	0.667	-0.0281	-0.1155	-2.2957	-0.1677
1.0	0.667	-0.0000	-0.4970	-3.1295	-0.0000
0.0	0.429	-1.1306	1.4604	0.2682	0.6259
0.1	0.429	-1.1939	1.2582	0.3567	0.4450
0.2	0.429	-1.1414	1.1340	0.3879	0.2611
0.3	0.429	-1.0089	1.0520	0.3405	0.0851
0.4	0.429	-0.8283	0.9804	0.1974	-0.0720
0.5	0.429	-0.6272	0.8915	-0.0549	-0.1991
0.6	0.429	-0.4293	0.7618	-0.4253	-0.2852
0.7	0.429	-0.2541	0.5716	-0.9190	-0.3194
0.8	0.429	-0.1172	0.3053	-1.5369	-0.2906
0.9	0.429	-0.0300	-0.0484	-2.2761	-0.1878
1.0	0.429	-0.0000	-0.4970	-3.1295	-0.0000
0.0	0.250	-0.7052	1.9075	0.1192	0.4769
0.1	0.250	-0.9330	1.6050	0.2066	0.3444
0.2	0.250	-0.9944	1.4163	0.2577	0.1927
0.3	0.250	-0.9363	1.2947	0.2424	0.0361
0.4	0.250	-0.8003	1.1984	0.1359	-0.1111
0.5	0.250	-0.6227	1.0913	-0.0812	-0.2347
0.6	0.250	-0.4341	0.9426	-0.4230	-0.3204
0.7	0.250	-0.2602	0.7269	-0.8982	-0.3541
0.8	0.250	-0.1210	0.4239	-1.5099	-0.3214
0.9	0.250	-0.0311	0.0191	-2.2562	-0.2081
1.0	0.250	-0.0000	-0.4970	-3.1295	-0.0000
0.0	0.111	-0.1745	2.4143	0.0298	0.2682
0.1	0.111	-0.5946	1.9923	0.0978	0.1991
0.2	0.111	-0.7912	1.7257	0.1557	0.0919
0.3	0.111	-0.8236	1.5551	0.1633	-0.0354
0.4	0.111	-0.7445	1.4278	0.0871	-0.1651
0.5	0.111	-0.5995	1.2984	-0.0993	-0.2795
0.6	0.111	-0.4273	1.1279	-0.4155	-0.3608
0.7	0.111	-0.2597	0.8847	-0.8743	-0.3913
0.8	0.111	-0.1217	0.5437	-1.4814	-0.3532
0.9	0.111	-0.0314	0.0869	-2.2358	-0.2286
1.0	0.111	-0.0000	-0.4970	-3.1295	-0.0000

BIBLIOGRAPHY

(1) J.F. COUNSELL, E.B. LEES and P.J. SPENCER, "Metallurgical Chemistry", Proc. Symp. Brunel Univ., and N.P.L., 1971, Ed. O. KUBASCHEWSKI, HMSO, U.K.

(2) A.J. BRADLEY, W.F. COX and H.J.GOLDSCHMIDT, J. Inst. Met., 1971, 67, 189.

(3) L. ELDFORD, F. MÜLLER and O. KUBASCHEWSKI, Berich. Bunsen., 1969, 73, 601.

(4) O. KUBASCHEWSKI, private communication.

Ga-Sn-Zn

I - EXPERIMENTAL RESULTS.-

The heats of mixing of the liquid solutions have been measured by microcalorimetry[1] à 723 K for :

$$0 < x_{Zn} < 1 \quad ; \quad x_{Ga}/x_{Sn} = 1/3 \; ; \; 1/1 \; ; \; 3/1$$

and $$0 < x_{Sn} < 1 \quad ; \quad x_{Ga}/x_{Zn} = 1/3 \; ; \; 1/1 \; ; \; 3/1$$

The partial free energies were measured by DANILIN[2] using an e.m.f. method in the temperature range 713-813 K for :

$$0 < x_{Zn} < 1 \quad ; \quad x_{Ga}/x_{Sn} = 1/4 \; ; \; 1/1 \; ; \; 7/3 \; ; \; 9/1$$

The phase diagram was determined by EVANS[3].

II - COMPARISON BETWEEN EXPERIMENTAL AND CALCULATED THERMODYNAMIC DATA.-

a) Binary solutions :

Ga-Zn[4]

$$\begin{cases} \Delta H_M = x_{Zn}(1-x_{Zn})(420x_{Zn}^2 + 478x_{Zn} + 1413) \\ \Delta S_M^{xs} = x_{Zn}(1-x_{Zn})(-9.18456\,x_{Zn}^3 + 13.08382\,x_{Zn}^2 \\ \qquad - 5.35968\,x_{Zn} + 2.49791) \end{cases} \quad (1)$$

Sn-Zn[6]

$$\begin{cases} \Delta H_M = x_{Zn}(1-x_{Zn})(2418\,x_{Zn}^2 - 21x_{Zn} + 2509) \\ \Delta S^{xs} = x_{Zn}(1-x_{Zn})(0.8317\,x_{Zn}^2 - 0.12326\,x_{Zn} + 1.8429) \end{cases} \quad (2)$$

Ga-Sn[5]

$$\begin{cases} \Delta H_M = x_{Sn}(1-x_{Sn})(108.318\,x_{Sn}^2 - 232.54\,x_{Sn} + 916.7) \\ \Delta S^{xs} = x_{Sn}(1-x_{Sn})\,0.25 \end{cases} \quad (3)$$

b) Ternary solutions:

1) Heats of mixing :

The experimental values[1] of the heats of mixing were fitted by the following equation :

$$\Delta H_M = (x_{Zn} + x_{Ga})^2 [\Delta H_{Ga-Zn}] x_{Ga}/x_{Zn} + (x_{Zn} + x_{Sn})^2 [\Delta H_{Sn-Zn}] x_{Sn}/x_{Zn}$$

$$+ (x_{Ga} + x_{Sn}) [\Delta H_{Ga-Sn}] x_{Ga}/x_{Sn} + x_{Ga} x_{Sn} x_{Zn} [\lambda x_{Zn} + \nu x_{Ga} + \mu x_{Sn}] \qquad (4)$$

which yields :

λ = - 4147.28

ν = 849.46

μ = 216.56

Table 1 presents the experimental and calculated results. The differences observed are, for that case, and except for three points, with the experimental errors.

2) Excess, entropies of mixing :

The excess entropies of mixing have been calculated by an equation similar to (4) with λ, ν, $\mu = 0$

Table I

x_{Ga}/x_{Sn} / x_{Zn}	1/3		1/1		3/1	
	exp	exp-calc	exp	exp-calc	exp	exp-calc
0.1	355	37	355	6	290	- 6
0.2	515	43	490	19	395	- 11
0.3	635	41	590	26	470	- 21
0.4	710	29	655	21	535	1
0.5	740	5	685	20	560	- 30
0.6	740	6	675	4	540	- 50
0.7	680	-15	605	-24	480	- 67
0.8	560	-27	475	-50	380	- 61
0.9	360	-16	280	-41	240	- 19

x_{Ga}/x_{Zn} / x_{Sn}	1/3		1/1		3/1	
	exp	exp-calc	exp	exp-calc	exp	exp-calc
0.1	570	- 7	570	19	375	1
0.2	690	8	605	11	420	12
0.3	730	10	610	12	425	- 6
0.4	720	9	585	8	400	- 12
0.5	695	30	530	- 5	365	- 22
0.6	590	2	455	- 18	315	- 30
0.7	475	- 9	360	- 29	255	- 31
0.8	335	- 17	250	- 33	275	- 34
0.9	170	- 28	130	- 23	90	- 23

The calculated partial free energies of Zn at 723 K are compared to DANILIN's measurements in Table II

Table II

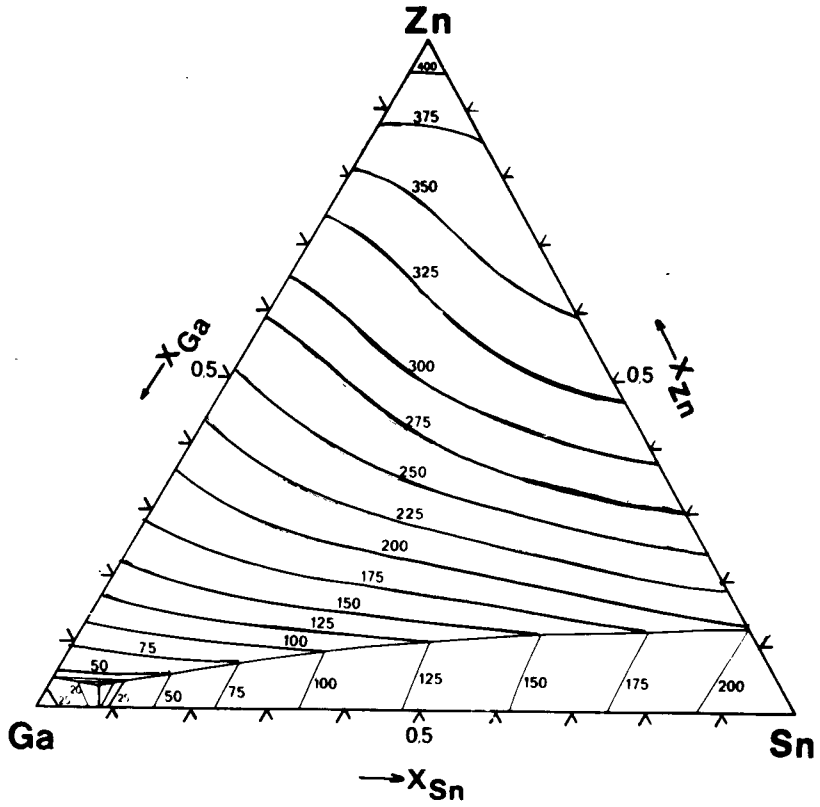
y_{Ga}/y_{Sn} / y_{Zn}	1/4		1/1		7/3		9/1	
	exp	exp-calc	exp	exp-calc	exp	exp-calc	exp	exp-calc
0.1	- 2538	- 25	- 2644	143	- 2681	216	- 2883	113
0.4	- 764	- 110	- 953	- 44	- 963	+ 69	- 1019	107
0.6	- 365	- 104	- 476	- 96	- 582	- 105	- 567	4
0.8	- 198	- 52	- 245	- 75	- 264	- 79	- 274	- 73
0.9	- 119	- 19	- 124	- 19	- 133	- 28	- 137	- 33

III - COMPARISON BETWEEN THE EXPERIMENTAL AND CALCULATED PHASE DIAGRAM.-

The Ga-Sn, Ga-Zn and Zn-Sn phases diagrams are simple eutectic-type with no appreciable solid solution except in the Sn rich corner in the Sn-Zn system. The liquidus points of the ternary system are compared to the experimental results[3] in Table III. The agreement is very satisfactory except in the Ga rich corner. A calculated diagram is shown in figure 1.

TABLE III

x_{Ga}	x_{Sn}	x_{Zn}	exp	exp-calc
		liq ⇄ Zn		
0.833	0.067	0.100	357	- 1
0.819	0.045	0.136	383	2
0.804	0.024	0.172	396	- 4
0.670	0.181	0.149	398	1
0.662	0.162	0.176	414	3
0.283	0.597	0.120	420	- 4
0.493	0.343	0.164	421	9
0.575	0.229	0.196	430	8
0.486	0.321	0.194	436	10
0.279	0.572	0.149	438	11
0.556	0.183	0.261	455	6
0.270	0.515	0.215	472	14
0.539	0.139	0.322	476	7
0.261	0.460	0.279	498	15
		liq ⇄ Ga		
0.873	0.045	0.082	286	1
0.867	0.047	0.086	292.5	21.5
0.911	0.024	0.065	295	22
0.916	0.030	0.054	296	9
0.956	0.012	0.032	297	14
0.924	0.012	0.064	300	29
0.954	0.024	0.022	300	13
		liq ⇄ Sn		
0.845	0.087	0.068	299	4
0.859	0.107	0.034	305	0
0.691	0.223	0.086	350	9
0.710	0.264	0.026	357	1
0.528	0.458	0.014	360	2
0.509	0.396	0.095	386	0
0.516	0.416	0.068	388	- 1
0.522	0.436	0.042	390	- 2
0.528	0.458	0.014	395	1
0.286	0.622	0.092	422	- 5
0.292	0.611	0.047	430	- 2
0.297	0.687	0.016	436	0


Zn
400
375
350
325
300
275
250
225
200
175
150
125
100
75
50
X_{Ga}
0.5
X_{Zn}
0.5
Ga
0.5
Sn
X_{Sn}

IV - PARTIAL AND INTEGRAL HEATS OF MIXING FOR LIQUID GA-SN-ZN SOLUTIONS AT 723K (CAL/MOL)

X ZN	XGA/XSN	DH ZN	DH GA	DH SN	DH
0.0	9.000	1513	11	707	81
0.1	9.000	1350	13	769	215
0.2	9.000	1157	39	884	330
0.3	9.000	958	93	1066	420
0.4	9.000	768	181	1305	483
0.5	9.000	586	313	1605	514
0.6	9.000	415	504	1985	510
0.7	9.000	260	773	2470	465
0.8	9.000	129	1145	3093	371
0.9	9.000	36	1646	3891	219
1.0	9.000	0	2311	4906	0
0.0	4.000	1608	41	535	140
0.1	4.000	1382	40	590	273
0.2	4.000	1208	63	653	387
0.3	4.000	1020	110	784	477
0.4	4.000	826	187	998	540
0.5	4.000	635	307	1304	571
0.6	4.000	452	486	1714	564
0.7	4.000	284	746	2248	513
0.8	4.000	141	1115	2934	408
0.9	4.000	39	1624	3806	241
1.0	4.000	0	2311	4906	0
0.0	2.333	1700	88	395	180
0.1	2.333	1412	81	454	315
0.2	2.333	1241	99	514	427
0.3	2.333	1069	135	620	517
0.4	2.333	883	199	808	582
0.5	2.333	689	303	1098	615
0.6	2.333	495	468	1510	609
0.7	2.333	312	718	2065	555
0.8	2.333	155	1084	2792	444
0.9	2.333	43	1601	3725	263
1.0	2.333	0	2311	4906	0
0.0	1.500	1793	149	282	202
0.1	1.500	1455	132	345	341
0.2	1.500	1276	139	412	454
0.3	1.500	1115	163	512	546
0.4	1.500	938	211	681	614
0.5	1.500	743	299	951	651
0.6	1.500	540	449	1351	648
0.7	1.500	343	689	1912	594
0.8	1.500	172	1052	2665	477
0.9	1.500	48	1577	3648	284
1.0	1.500	0	2311	4906	0

0.0	1.000	1887	222	191	207
0.1	1.000	1517	193	255	353
0.2	1.000	1323	184	332	471
0.3	1.000	1164	190	432	567
0.4	1.000	992	220	589	639
0.5	1.000	797	291	841	681
0.6	1.000	586	426	1225	682
0.7	1.000	376	657	1782	629
0.8	1.000	189	1018	2550	508
0.9	1.000	53	1553	3576	304
1.0	1.000	0	2311	4906	0
0.0	0.667	1987	309	121	196
0.1	0.667	1599	260	183	353
0.2	0.667	1386	230	265	478
0.3	0.667	1220	215	367	581
0.4	0.667	1047	226	517	659
0.5	0.667	850	280	753	707
0.6	0.667	631	401	1121	712
0.7	0.667	409	623	1668	661
0.8	0.667	208	983	2446	538
0.9	0.667	59	1528	3506	324
1.0	0.667	0	2311	4906	0
0.0	4.286	1598	37	552	134
0.1	4.286	1379	37	607	268
0.2	4.286	1204	60	672	381
0.3	4.286	1014	107	807	472
0.4	4.286	820	186	1024	535
0.5	4.286	630	307	1331	565
0.6	4.286	448	488	1740	559
0.7	4.286	281	749	2270	508
0.8	4.286	139	1118	2950	404
0.9	4.286	39	1626	3815	239
1.0	4.286	0	2311	4906	0
0.0	2.500	1687	80	413	175
0.1	2.500	1407	74	472	310
0.2	2.500	1236	93	531	422
0.3	2.500	1062	132	639	512
0.4	2.500	875	197	830	577
0.5	2.500	681	304	1123	610
0.6	2.500	489	471	1536	603
0.7	2.500	308	722	2089	549
0.8	2.500	153	1088	2811	439
0.9	2.500	43	1604	3736	260
1.0	2.500	0	2311	4906	0
0.0	0.111	2353	647	8	72
0.1	0.111	1958	519	44	278
0.2	0.111	1671	414	111	447
0.3	0.111	1446	328	204	585
0.4	0.111	1236	270	337	693
0.5	0.111	1013	260	543	764
0.6	0.111	767	329	872	788
0.7	0.111	509	517	1390	747
0.8	0.111	265	873	2174	621
0.9	0.111	77	1451	3313	382
1.0	0.111	0	2311	4906	0

PARTIAL AND INTEGRAL EXCESS ENTROPIES OF MIXING FOR LIQUID GA-SN-ZN SOLUTIONS AT 723K (CAL/MOL)/K

X ZN	XGA/XSN	SXS ZN	SXS GA	SXS SN	SXS
0.0	9.000	2.4099	0.0025	0.2025	0.0225
0.1	9.000	1.4361	0.0528	0.1819	0.2027
0.2	9.000	1.0927	0.1078	0.2557	0.3166
0.3	9.000	0.9474	0.1466	0.3845	0.4035
0.4	9.000	0.7985	0.2190	0.5502	0.4706
0.5	9.000	0.5896	0.3888	0.7566	0.5076
0.6	9.000	0.3491	0.6892	1.0163	0.4982
0.7	9.000	0.1387	1.0872	1.3387	0.4308
0.8	9.000	0.0126	1.4574	1.7211	0.3068
0.9	9.000	-0.0160	1.5621	2.1411	0.1476
1.0	9.000	-0.0000	1.0375	2.5514	0.0000
0.0	4.000	2.3269	0.0100	0.1600	0.0400
0.1	4.000	1.4073	0.0625	0.1474	0.2123
0.2	4.000	1.1276	0.1069	0.2006	0.3261
0.3	4.000	0.9918	0.1386	0.3006	0.4172
0.4	4.000	0.8196	0.2203	0.4468	0.4872
0.5	4.000	0.5867	0.4110	0.6486	0.5226
0.6	4.000	0.3385	0.7251	0.9168	0.5085
0.7	4.000	0.1356	1.1103	1.2560	0.4367
0.8	4.000	0.0188	1.4389	1.6593	0.3117
0.9	4.000	-0.0101	1.5067	2.1042	0.1535
1.0	4.000	-0.0000	1.0375	2.5514	0.0000
0.0	2.333	2.2489	0.0225	0.1225	0.0525
0.1	2.333	1.3845	0.0750	0.1200	0.2181
0.2	2.333	1.1568	0.1079	0.1682	0.3321
0.3	2.333	1.0234	0.1369	0.2510	0.4268
0.4	2.333	0.8287	0.2342	0.3804	0.4983
0.5	2.333	0.5785	0.4469	0.5733	0.5317
0.6	2.333	0.3297	0.7677	0.8417	0.5138
0.7	2.333	0.1368	1.1290	1.1880	0.4398
0.8	2.333	0.0278	1.4094	1.6037	0.3158
0.9	2.333	-0.0040	1.4444	2.0684	0.1596
1.0	2.333	-0.0000	1.0375	2.5514	0.0000
0.0	1.500	2.1759	0.0400	0.0900	0.0600
0.1	1.500	1.3740	0.0897	0.0961	0.2204
0.2	1.500	1.1860	0.1100	0.1434	0.3359
0.3	1.500	1.0424	0.1427	0.2169	0.4334
0.4	1.500	0.8249	0.2622	0.3355	0.5049
0.5	1.500	0.5652	0.4957	0.5205	0.5354
0.6	1.500	0.3231	0.8130	0.7851	0.5146
0.7	1.500	0.1425	1.1383	1.1318	0.4405
0.8	1.500	0.0393	1.3658	1.5532	0.3196
0.9	1.500	0.0024	1.3744	2.0337	0.1660
1.0	1.500	-0.0000	1.0375	2.5514	0.0000

0.0	1.000	2.1079	0.0625	0.0625	0.0625
0.1	1.000	1.3783	0.1058	0.0753	0.2193
0.2	1.000	1.2153	0.1141	0.1221	0.3375
0.3	1.000	1.0477	0.1596	0.1913	0.4371
0.4	1.000	0.8089	0.3071	0.3045	0.5070
0.5	1.000	0.5488	0.5554	0.4839	0.5342
0.6	1.000	0.3204	0.8548	0.7427	0.5118
0.7	1.000	0.1531	1.1313	1.0849	0.4396
0.8	1.000	0.0529	1.3042	1.5069	0.3234
0.9	1.000	0.0089	1.2959	1.9999	0.1728
1.0	1.000	0.0000	1.0375	2.5514	0.0000
0.0	0.667	2.0449	0.0900	0.0400	0.0600
0.1	0.667	1.3993	0.1222	0.0576	0.2150
0.2	0.667	1.2405	0.1230	0.1034	0.3371
0.3	0.667	1.0373	0.1938	0.1717	0.4376
0.4	0.667	0.7832	0.3705	0.2839	0.5044
0.5	0.667	0.5332	0.6197	0.4596	0.5284
0.6	0.667	0.3237	0.8821	0.7111	0.5060
0.7	0.667	0.1687	1.0986	1.0451	0.4380
0.8	0.667	0.0683	1.2197	1.4638	0.3278
0.9	0.667	0.0153	1.2080	1.9667	0.1801
1.0	0.667	0.0000	1.0375	2.5514	0.0000
0.0	4.286	2.3356	0.0089	0.1644	0.0383
0.1	4.286	1.4103	0.0613	0.1506	0.2114
0.2	4.286	1.1243	0.1069	0.2050	0.3252
0.3	4.286	0.9876	0.1391	0.3075	0.4160
0.4	4.286	0.8179	0.2195	0.4558	0.4857
0.5	4.286	0.5873	0.4080	0.6584	0.5213
0.6	4.286	0.3396	0.7209	0.9262	0.5076
0.7	4.286	0.1357	1.1080	1.2642	0.4362
0.8	4.286	0.0180	1.4414	1.6656	0.3112
0.9	4.286	-0.0108	1.5130	2.1081	0.1528
1.0	4.286	-0.0000	1.0375	2.5514	0.0000
0.0	2.500	2.2597	0.0204	0.1276	0.0510
0.1	2.500	1.3871	0.0731	0.1237	0.2175
0.2	2.500	1.1527	0.1077	0.1722	0.3314
0.3	2.500	1.0196	0.1368	0.2569	0.4256
0.4	2.500	0.8282	0.2314	0.3883	0.4970
0.5	2.500	0.5800	0.4410	0.5825	0.5307
0.6	2.500	0.3308	0.7613	0.8511	0.5133
0.7	2.500	0.1363	1.1268	1.1969	0.4395
0.8	2.500	0.0264	1.4144	1.6113	0.3152
0.9	2.500	-0.0049	1.4537	2.0735	0.1587
1.0	2.500	-0.0000	1.0375	2.5514	0.0000
0.0	0.111	1.8859	0.2025	0.0025	0.0225
0.1	0.111	1.5039	0.1944	0.0210	0.1849
0.2	0.111	1.1995	0.2957	0.0694	0.3135
0.3	0.111	0.9460	0.4116	0.1501	0.4072
0.4	0.111	0.7355	0.4997	0.2663	0.4680
0.5	0.111	0.5512	0.5650	0.4270	0.4960
0.6	0.111	0.3854	0.6213	0.6467	0.4889
0.7	0.111	0.2385	0.6832	0.9445	0.4425
0.8	0.111	0.1170	0.7644	1.3434	0.3507
0.9	0.111	0.0323	0.8782	1.8695	0.2061
1.0	0.111	0.0000	1.0375	2.5514	0.0000

BIBLIOGRAPHY

(1) M. GAMBINO, J.P. BROS and I. ANSARA, Rev. Int. Htes Temp. et Réfract., 1973, 10, 1, 5.

(2) N.V. DANILIN, S.P. YATSENKO, V.J. KONONENKO and BRUZHJINA, "Propriétés du Gallium en solution et sous forme d'alliages", p. 83, Inst. Khim. Akad. Nauk SSSR, Ural. Fil., USSR.

(3) R. EVANS and R. JOFFEE, Trans. Met. Soc. AIME, 1952, 296, 163.

(4) J.P. BROS and M. LAFFITTE, J. Chim. Phys., 1970, 67, 1636.

(5) M. GAMBINO, J.P. BROS and I. ANSARA, Colloque International du CNRS "Thermochimie", Marseille, 1971, 201.

(6) R. HULTGREN, P.D. DESRE, D.T. HAWKINS, M. GLEISER and K.K. KELLY, "Selected Values of the Thermodynamic Properties of Binary Alloys", 1973, Amer. Soc. Metals, Metals Park, Ohio, USA.

Imprimeur : Ecole Nationale Supérieure
d'Electrochimie et d'Electrométallurgie
Domaine Universitaire

38 - SAINT MARTIN D'HERES